PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-133556

(43)Date of publication of application : 12.05.2000

(51)Int.Cl. H01G 9/04
H01G 9/028

(21)Application number : 10-302254

(22)Date of filing : 23.10.1998

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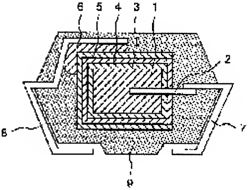
(54) SOLID ELECTROLYTIC CAPACITOR AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a solid electrolytic capacitor with satisfactory characteristics that can significantly reduce the current leakage.

SOLUTION: In a solid electrolytic capacity, having an anode 1 made of valve action metal, a dielectric oxide film 3 formed on the surface of the anode 1 through anode oxidation and a conductive polymer layer (solid electrolyte) 5 provided on the dielectric oxide film 3, an insulating layer 4 in particular with a resistivity of 1012 Ω cm or more is provided between the dielectric oxide film 3 and the solid electrolytic layer 5.



LEGAL STATUS

[Date of request for examination]	20.10.2005
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	
[Date of registration]	
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] The solid electrolytic capacitor characterized by preparing an insulating layer between said dielectric oxide films and solid electrolytes in the solid electrolytic capacitor equipped with the solid electrolyte on the anode plate which consists of a valve action metal, the dielectric oxide film formed in the front face of this anode plate of anodic oxidation, and this dielectric oxide film.
[Claim 2] The solid electrolytic capacitor characterized by specific resistance preparing the insulating layer more than 1012-ohmcm between said dielectric oxide films and solid electrolytes in the solid electrolytic capacitor equipped with the solid electrolyte on the anode plate which consists of a valve action metal, the dielectric oxide film formed in the front face of this anode plate of anodic oxidation, and this dielectric oxide film.
[Claim 3] The solid electrolytic capacitor according to claim 1 or 2 with which said insulating layer is formed with either an epoxy resin, polyimide resin, silicone resin, an unsaturated polyester resin, polystyrene resin, phenol resin, synthetic rubber, thermoplastic elastomer, such mixture or a copolymer.
[Claim 4] The solid electrolytic capacitor according to claim 1 or 2 formed by the inorganic polymer in which said insulating layer includes Si-O-Si association, or inorganic polymer including aluminum-O-aluminum association.
[Claim 5] The solid electrolytic capacitor according to claim 1, 2, or 4 with which said solid electrolyte is formed with either the poly aniline, the poly aniline derivative, Pori (p-phenylene), the Pori (p-phenylene) derivative, the poly vinylene, the poly vinylene derivative, polypyrrole, a polypyrrole derivative, the poly thiophene or the poly thiophene derivative.
[Claim 6] In the manufacture approach of a solid electrolytic capacitor equipped with the anode plate which consists of a valve action metal, the dielectric oxide film formed in the front face of this anode plate, and the solid electrolyte formed on this dielectric oxide film The 1st process which anodizes the front face of said anode plate and forms said dielectric oxide film, the [which forms an insulating layer after forming a solid electrolyte on the 2nd process which forms an insulating layer on said dielectric oxide film, or said dielectric oxide film] -- the manufacture approach of the solid electrolytic capacitor characterized by having 2' processes and the 3rd process which forms said solid electrolyte on said insulating layer.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to the solid electrolytic capacitor which was equipped with the dielectric oxide film formed of anodic oxidation on the surface of the anode plate with respect to a solid electrolytic capacitor and its manufacture approach, and is equipped with the solid electrolyte on the dielectric oxide film of a parenthesis, and its manufacture approach.
[0002]
[Description of the Prior Art] Conventionally, usually in the solid electrolytic capacitor which formed the anode plate with the valve action metal, for example, a tantalum and aluminum, formed the dielectric oxide film in this anode plate front face by anodic oxidation, and formed the solid electrolyte in that dielectric oxide film front face, 8 and 8'-tetracyano quinodimethan (TCNQ) complex salt were used [a manganese dioxide (MnO2), 7 and 7', and] for the solid electrolyte until now.
[0003] However, since electric conductivity of a manganese dioxide is not enough, the impedance of the solid electrolytic capacitor in a high frequency cannot be reduced enough, and it is easy to pyrolyze TCNQ complex salt, and also has the fault that the thermal resistance of a solid electrolytic capacitor is inadequate.
[0004] In order to cancel such fault, in recently, the conductive polymer which is high conductivity and excelled the manganese dioxide in thermal resistance, for example, the solid electrolytic capacitor which used polypyrrole and the poly aniline for the solid electrolyte, is being developed.
[0005]
[Problem(s) to be Solved by the Invention] By the way, usually it is manufactured according to the chemistry oxidation polymerization of an aniline, and the electric conductivity of the poly aniline manufactured according to the chemistry oxidation polymerization reaches 2.0 S/cm extent as this poly aniline is indicated by JP,61-258831,A. However, since the poly aniline obtained by doing in this way is insoluble and infusible nature, it cannot create the poly aniline solution, with conductivity maintained. Therefore, after compounding the poly aniline which has conductivity, it is difficult to apply it to the solid electrolyte of a solid electrolytic capacitor.
[0006] By the way, in the solid electrolytic capacitor which manufactures the poly aniline of a solid electrolyte by the chemistry oxidation-polymerization method, the approach of forming the poly aniline by the chemistry oxidation-polymerization reaction on a dielectric oxide-film front face is used by sinking in by turns the anode plate which formed the dielectric oxide film in the oxidizer solution (the 1st solution) which oxidizes an aniline, and the aniline solution (the 2nd solution) containing the proton acid which is a dopant. In this case, there is no formation approach of this poly aniline in the 1st solution and the 2nd solution with how many times by turns and it needs to sink in repeatedly the anode plate in which the dielectric oxide film was formed on the front face to make electrostatic capacity of a solid electrolytic capacitor into desired magnitude.
[0007] When using a metal tantalum for an anode plate as a valve action metal especially, sinter the tantalum powder which carried out pressing and a sintered compact is formed. Since the sintered

compact is used as an anode plate, when an anode plate is infiltrated into the 1st solution and the 2nd solution by turns, It is difficult for fully infiltrating an aniline, a dopant, and an oxidizing agent to the interior of an anode plate to obtain the solid electrolytic capacitor in which the capacity incidence of a solid electrolytic capacitor will become small, and has necessary electrostatic capacity difficultly consequently.

[0008] Moreover, it is the problem of leakage current especially to become a problem with this kind of solid electrolytic capacitor. Namely, although the dielectric oxide film which sintered the tantalum powder which carried out pressing, formed the sintered compact, and anodized the sintered compact is used as a dielectric when a metal tantalum is used for an anode plate as a valve action metal The specific resistance of the dielectric oxide film is about 1011-ohmcm, and the surface area of a dielectric oxide film is 2 about 10cm 2-1000cm. about 500microA Since the thickness of a dielectric oxide film is about 20nm - 200nm, resistance of a solid electrolytic capacitor serves as abbreviation 100kohm at the maximum, and the leakage current in that case will flow that it is small. Thus, in the conventional solid electrolytic capacitor, leakage current had had the bad influence on the property of a solid electrolytic capacitor greatly.

[0009] Compared with the conventional solid electrolytic capacitor, the place which this invention was made in view of this, and is made into the purpose can reduce leakage current sharply, and is to offer a solid-state electrolytic capacitor with a good property.

[0010]

[Means for Solving the Problem] In order to develop that to which this invention person etc. has the large capacity incidence as a solid electrolytic capacitor, and equivalent series resistance and leakage current become small, It is what that the direct conductivity matter contacts the front face of the dielectric oxide film formed by anodic oxidation by making a metal tantalum into an anode plate as a result of inquiring energetically showed clearly that it is the cause of property degradation of leakage current, and resulted in this invention. An insulating layer is formed between a dielectric oxide film and a solid electrolyte, and a solid electrolytic capacitor is formed in it.

[0011] That is, in the solid electrolytic capacitor equipped with the solid electrolyte on the anode plate which consists of a valve action metal, the dielectric oxide film formed in the front face of this anode plate of anodic oxidation, and this dielectric oxide film, this invention prepares an insulating layer between said dielectric oxide films and solid electrolytes, and attains the desired end.

[0012] Moreover, in the solid electrolytic capacitor equipped with the solid electrolyte on the anode plate where this invention consists of a valve action metal, the dielectric oxide film formed in the front face of this anode plate of anodic oxidation, and this dielectric oxide film, specific resistance prepares the insulating layer more than 1012-ohmcm between said dielectric oxide films and solid electrolytes.

[0013] Moreover, said insulating layer is formed in this case with either an epoxy resin, polyimide resin, silicone resin, an unsaturated polyester resin, polystyrene resin, phenol resin, synthetic rubber, thermoplastic elastomer, such mixture or a copolymer. Moreover, it is made to form by the inorganic polymer which includes Si-O-Si association for said insulating layer, or inorganic polymer including aluminum-O-aluminum association.

[0014] Moreover, said solid electrolyte is formed with either the poly aniline, the poly aniline derivative, Pori (p-phenylene), the Pori (p-phenylene) derivative, the poly vinylene, the poly vinylene derivative, polypyrrole, a polypyrrole derivative, the poly thiophene or the poly thiophene derivative.

[0015] Moreover, the anode plate where this invention consists of a valve action metal and the dielectric oxide film formed in the front face of this anode plate, Manufacture of a solid electrolytic capacitor equipped with the solid electrolyte formed on this dielectric oxide film is faced. The 1st process which anodizes the front face of said anode plate and forms said dielectric oxide film, the [which forms an insulating layer after forming a solid electrolyte on the 2nd process which forms an insulating layer on said dielectric oxide film, or said dielectric oxide film] -- it is made to have 2' processes and the 3rd process which forms said solid electrolyte on said insulating layer

[0016] Namely, since the insulating layer is prepared between the dielectric oxide film and the solid electrolyte as it is the solid electrolytic capacitor formed in this way, by this insulating layer, it can be

lost that the direct conductivity matter contacts the front face of the dielectric oxide film formed by anodic oxidation, therefore it can reduce leakage current sharply compared with this known kind of solid electrolytic capacitor, and can use it as the solid-state electrolytic capacitor with a good property.
[0017]
[Embodiment of the Invention] In the gestalt of one operation of this invention a solid electrolytic capacitor The anode plate which consists of a valve action metal, and the dielectric oxide film formed in the front face of an anode plate by anodic oxidation, It has an insulating layer between the conductive polymer layer formed on the dielectric oxide film, and a dielectric oxide film and a conductive polymer layer. A conductive polymer layer The poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), or the Pori (p-phenylene) derivative, Or it is the poly vinylene or the poly vinylene derivative, and specific resistance of an insulating layer is a thing more than 1016-ohmcm preferably more than 1012-ohmcm.
[0018] In the gestalt of other operations of this invention the manufacture approach of a solid electrolytic capacitor The anode plate which consists of a valve action metal, and the dielectric oxide film formed in the front face of an anode plate by anodic oxidation, It is the manufacture approach of the insulating layer formed on the dielectric oxide film, and the solid electrolytic capacitor equipped with the conductive polymer layer on the insulating layer. The 1st process which anodizes the front face of an anode plate and forms a dielectric oxide film, the 2nd process which forms an insulating layer on a dielectric oxide film, On an insulating layer, the poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or it is manufactured respectively through the 3rd process which forms the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), the Pori (p-phenylene) derivative, the poly vinylene, or the poly vinylene derivative.
[0019] The insulating layers formed at the 2nd process are an epoxy resin, phenol resin, polyimide, polystyrene, silicon resin, an unsaturated polyester resin, and synthetic rubber that specific resistance should just be more than 1016-ohmcm preferably more than 1012-ohmcm. In order to form an insulating layer in homogeneity to the interior of a solid electrolytic capacitor component, viscosity is small and the wettability good thing to a dielectric oxide film is desirable.
[0020] The insulating material solution which has the polymerization degree of extent which dissolves the formation approach of the insulating material in the 2nd process in a solvent, In the case of an epoxy resin insulator layer, for example, the bisphenol A mold epoxy resin solution, In the case of a phenol resin insulator layer, in the case of a phenol formaldehyde solution and a polyimide insulator layer, a diamine solution and an acid-anhydride solution, In the case of a silicone resin insulator layer, in the case of an alkoxysilane solution and an unsaturated-polyester-resin insulator layer, a fumaric-acid solution, ethylene glycol, and a styrene solution, In the case of an inorganic polymer insulator layer including Si-O-Si association, a silanol solution, In the case of an inorganic polymer insulator layer including aluminum-O-aluminum association, an alkoxy aluminum solution etc. is adjusted. A dielectric oxide film is immersed in each solution, it heat-treats if needed, the polymerization reaction of an insulating layer is advanced, and specific resistance forms the insulating layer more than 1016-ohmcm on a dielectric oxide film preferably more than 1012-ohmcm.
[0021] About means other than the aforementioned insulating stratification approach On a dielectric oxide film, the poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), or the Pori (p-phenylene) derivative, Or there is the approach of making insulation-ize a solid electrolyte and forming an insulating layer on a dielectric oxide film by forming the solid electrolyte which consists of poly vinylene or a poly vinylene derivative, and heat-treating above the temperature to which the dopant of a solid electrolyte evaporates.

[0022] This purpose can be attained also by inert gas ambient atmospheres, such as nitrogen, being sufficient, and carrying out in a vacuum ambient atmosphere besides performing heat treatment in air. Furthermore, if an insulating layer is formed by this approach, it will become possible to form a uniform insulating layer in a dielectric oxide film front face, and it will become possible to reduce leakage current sharply compared with this known kind of solid electrolytic capacitor.

[0023] In the gestalt of other operations of this invention the manufacture approach of a solid electrolytic capacitor the [which forms an insulating layer after forming a solid electrolyte on the 1st process which anodizes the front face of an anode plate and forms a dielectric oxide film, and a dielectric oxide film] -- 2' processes -- On an insulating layer, the poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or it is manufactured respectively through the 3rd process which forms the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), the Pori (p-phenylene) derivative, the poly vinylene, or the poly vinylene derivative.
[0024] the -- in 2' processes, by forming a solid electrolyte on a dielectric oxide film, the electrolytic polymerization reaction on a dielectric oxide film is attained, and an insulating layer is formed on a dielectric oxide film by the electrolytic polymerization reaction. In 2' processes, after forming a solid electrolyte on a dielectric oxide film, an electrolytic polymerization reaction is possible. the [therefore,] -- the monomer solution with which the specific resistance of the insulating layer formed of an electrolytic polymerization reaction becomes more than 1016-ohmcm preferably more than 1012-ohmcm -- adjusting -- the monomer solution -- the, after the dielectric oxide film which formed the solid electrolyte in the front face at 2' processes is immersed By impressing an electrical potential difference and carrying out electrolytic polymerization of the monomer, an insulating layer is formed on a dielectric oxide film.
[0025] The monomer solution is a solution which dissolved the compound which expresses with for example, amino diphenyl or drawing 2 which is represented by the amino benzophenone that the specific resistance of the insulating layer formed by electrolytic polymerization should just be more than 1016-ohmcm preferably more than 1012-ohmcm. According to this approach, by impressing the electric field impressed at the time of electrolytic polymerization to the whole dielectric oxide film, it becomes possible to form a uniform insulating layer in a dielectric oxide-film front face, and it becomes possible to reduce leakage current sharply compared with this known kind of solid electrolytic capacitor.
[0026] This invention is explained to a detail based on the example illustrated below.
[0027] [Example 1] Drawing 1 is the sectional view showing the configuration of one example of the solid electrolytic capacitor by this invention, and shows the example of the tantalum condenser which constituted the anode plate from a sintered compact of a metal tantalum. the anode plate where 1 consists of impalpable powder of a tantalum in drawing 1 , and 2 -- an anode plate lead and 3 -- for a conductive polymer layer and 6, as for an anode terminal and 8, a silver larer and 7 are [a dielectric oxide film and 4 / an insulating layer and 5 / a cathode terminal and 9] sheathing.
[0028] Namely, as for the solid electrolytic capacitor by this invention, the insulating layer 4 is formed between the dielectric oxide film 3 and the conductive polymer layer (solid electrolyte) 5. In addition, as for this insulating layer, specific resistance is formed more than 1012-ohmcm.
[0029] It is as follows when here describes the circumstances in the production process of the solid electrolytic capacitor (tantalum condenser) of this example 1.
[0030] First, it changes into the condition of having inserted in the end section of the anode plate lead 2 into the impalpable powder of a metal tantalum, and pressing is carried out, the acquired Plastic solid is sintered by high temperature in a vacuum, and the anode plate 1 which consists of a sintered compact is formed (the 1st process).
[0031] Next, the anode plate 1 obtained at the 1st process is immersed into an aqua-fortis water solution, chemical conversion is performed after that, and the dielectric oxide film 3 of rated 7V10micro F is formed in anode plate 1 front face (the 2nd process).
[0032] Subsequently, a 0.01M4 and 4'-diamino diphenyl ether NMP (N-methyl-2-pyrrolidone) solution and the NMP solution of 0.01M biphenyl tetracarboxylic dianhydride are adjusted, respectively. Specific resistance forms the insulating layer 4 which consists of polyimide which is about 1016-ohmcm on scaling anode plate 1 front face by heating the anode plate 1 (this being hereafter called scaling anode plate 1) which formed the dielectric oxide film 3 according to the 2nd process at 150 degrees C, after being immersed in each solution by turns (the 3rd process).
[0033] Then, a 0.5M ammonium-peroxydisulfate water solution is adjusted, and the scaling anode plate 1 which formed the insulating layer 4 according to the 3rd process is immersed in a 0.5M ammonium-

peroxydisulfate water solution for 10 seconds (the 4th process).
[0034] Next, an equivalent aniline and the water solution of p-phenolsulfonic acid adjust the aniline solution whose concentration is 0.5M. And 30 minutes after the 0.5M ammonium-peroxydisulfate water solution in the 4th process is immersed, the scaling anode plate 1 is immersed in an aniline solution for 10 seconds (the 5th process).
[0035] Subsequently, after the aniline solution in the 5th process is immersed, the scaling anode plate 1 is held at 50 degrees C for 30 minutes, and a chemistry oxidation-polymerization reaction is produced on the scaling anode plate 1 (the 6th process).
[0036] Furthermore, to the scaling anode plate 1 which carried out the circumstances of the 6th process, immersion to said ammonium-peroxydisulfate water solution and immersion to said aniline solution are performed by a unit of 20 times by turns, and the conductive polymer layer 5 obtained by the chemistry oxidation-polymerization reaction on the front face of the scaling anode plate 1 is formed (the 7th process).
[0037] Then, a silver larer 6 is formed in the predetermined part of the scaling anode plate 1 which carried out the circumstances of the 7th process and formed the insulating layer 4 after applying carbon paste and a silver paste (the 8th process).
[0038] Next, an anode terminal 7 is connected conductively to the other end of the anode plate lead 2 by welding after the 8th process, and a cathode terminal 8 is connected to a silver larer 6 (the 9th process).
[0039] Then, after the 9th process is performed, except for the derivation edge of an anode terminal 7 and a cathode terminal 8, resin is applied to the whole by the mold method, and the solid electrolytic capacitor (tantalum condenser) covered with sheathing 9 is formed (the 10th process).
[0040] Here, Table 1 is a table in which impressing rated voltage 7V and showing the leakage current of 1 minute after about the solid electrolytic capacitor (tantalum condenser) of this example 1, and the solid electrolytic capacitor of the example 1 of a comparison separately formed in order to compare with this example 1. A leak current value shows the average of ten solid electrolytic capacitors.
[0041]
[Table 1]
表 1

種類	リーク電流
実施例 1	0.52 μA
実施例 2	0.35 μA
比較例 1	2.3mA

[0042] In Table 1, the leakage current of the solid electrolytic capacitor of this example 1 in which the insulating layer was formed serves as the range of 0.1-1microA, it is an average of 0.52microA, the leakage current of the example 1 of a comparison serves as the range of 1-5mA, and it is an average of 2.3mA. Thus, the leakage current of the solid electrolytic capacitor of this example 1 is reduced sharply.
[0043] By the way, the solid electrolytic capacitor of the example 1 of a comparison for a comparison with this example 1 is manufactured as follows.
[0044] First, in the production process of the solid electrolytic capacitor of this example 1, the solid electrolytic capacitor of the example 1 of a comparison excepts the process which forms an insulating layer 4, i.e., the 3rd process, and is manufactured respectively through the 4th process to the 2nd process and the 10th process from the 1st process.
[0045] [Example 2] Next, the circumstances in the production process of the solid electrolytic capacitor (tantalum condenser) of this example 2 are described. In this example 2, from the 1st process of said this example 1 to the 2nd process is carried out.
[0046] Then, to the scaling anode plate 1 which carried out the circumstances of the 2nd process, like the 7th process of said this example 1, immersion to a ammonium-peroxydisulfate water solution and

immersion to said aniline solution are performed by a unit of 5 times by turns, and the conductive polymer layer obtained by the chemistry oxidation-polymerization reaction on the front face of the scaling anode plate 1 is formed (the 3' process).
[0047] next, a 0.05M4-amino benzophenone solution -- adjusting -- the 3' -- after the scaling anode plate 1 which carried out the circumstances of the process and formed the conductive polymer layer is immersed, an insulating layer 4 is formed on the scaling anode plate 1 by impressing and carrying out electrolytic polymerization of the electrical potential difference to the scaling anode plate 1 (the 4' process).
[0048] subsequently, the 4' -- on the scaling anode plate 1 which carried out the circumstances of the process and formed the insulating layer 4, like the 7th process of said this example 1, immersion to a ammonium-peroxydisulfate water solution and immersion to said aniline solution are performed by a unit of 15 times by turns, and the conductive polymer layer 5 obtained by the front face of the scaling anode plate 1 by the chemistry oxidation-polymerization reaction is formed (the 7' process).
[0049] Subsequently, from the 8th process of said this example 1 to the 10th process is carried out.
[0050] In addition, about the solid electrolytic capacitor (tantalum condenser) of this example 2, rated voltage 7V are impressed to Table 1, and the leakage current of 1 minute after is shown in it. In this table, the leakage current of the solid electrolytic capacitor of this example 2 which formed the insulating layer by the electrolytic polymerization reaction serves as the range of 0.1-0.8microA, it is an average of 0.35microA, and it turns out that leakage current is decreasing sharply to the solid electrolytic capacitor and EQC of this example 1 mentioned above.
[0051] As many things have been explained above, it can be lost that the direct conductivity matter contacts the front face of the dielectric oxide film formed by anodic oxidation by this insulating layer 4 since the insulating layer 4 is formed between the dielectric oxide film 3 and the conductive polymer layer 5, i.e., a solid electrolyte, according to this invention, therefore leakage current can be reduced sharply.
[0052]
[Effect of the Invention] As explained above, according to this invention, compared with the conventional solid electrolytic capacitor, leakage current can be reduced sharply and this kind with a good property of solid electrolytic capacitor can be obtained.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] Especially this invention relates to the solid electrolytic capacitor which was equipped with the dielectric oxide film formed of anodic oxidation on the surface of the anode plate with respect to a solid electrolytic capacitor and its manufacture approach, and is equipped with the solid electrolyte on the dielectric oxide film of a parenthesis, and its manufacture approach.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] Conventionally, usually in the solid electrolytic capacitor which formed the anode plate with the valve action metal, for example, a tantalum and aluminum, formed the dielectric oxide film in this anode plate front face by anodic oxidation, and formed the solid electrolyte in that dielectric oxide film front face, 8 and 8'-tetracyano quinodimethan (TCNQ) complex salt were used [a manganese dioxide (MnO2), 7 and 7', and] for the solid electrolyte until now.
[0003] However, since electric conductivity of a manganese dioxide is not enough, the impedance of the solid electrolytic capacitor in a high frequency cannot be reduced enough, and it is easy to pyrolyze TCNQ complex salt, and also has the fault that the thermal resistance of a solid electrolytic capacitor is inadequate.
[0004] In order to cancel such fault, in recently, the conductive polymer which is high conductivity and excelled the manganese dioxide in thermal resistance, for example, the solid electrolytic capacitor which used polypyrrole and the poly aniline for the solid electrolyte, is being developed.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to this invention, compared with the conventional solid electrolytic capacitor, leakage current can be reduced sharply and this kind with a good property of solid electrolytic capacitor can be obtained.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the way, usually it is manufactured according to the chemistry oxidation polymerization of an aniline, and the electric conductivity of the poly aniline manufactured according to the chemistry oxidation polymerization reaches 2.0 S/cm extent as this poly aniline is indicated by JP,61-258831,A. However, since the poly aniline obtained by doing in this way is insoluble and infusible nature, it cannot create the poly aniline solution, with conductivity maintained. Therefore, after compounding the poly aniline which has conductivity, it is difficult to apply it to the solid electrolyte of a solid electrolytic capacitor.
[0006] By the way, in the solid electrolytic capacitor which manufactures the poly aniline of a solid electrolyte by the chemistry oxidation-polymerization method, the approach of forming the poly aniline by the chemistry oxidation-polymerization reaction on a dielectric oxide-film front face is used by sinking in by turns the anode plate which formed the dielectric oxide film in the oxidizer solution (the 1st solution) which oxidizes an aniline, and the aniline solution (the 2nd solution) containing the proton acid which is a dopant. In this case, there is no formation approach of this poly aniline in the 1st solution and the 2nd solution with how many times by turns and it needs to sink in repeatedly the anode plate in which the dielectric oxide film was formed on the front face to make electrostatic capacity of a solid electrolytic capacitor into desired magnitude.
[0007] When using a metal tantalum for an anode plate as a valve action metal especially, sinter the tantalum powder which carried out pressing and a sintered compact is formed. Since the sintered compact is used as an anode plate, when an anode plate is infiltrated into the 1st solution and the 2nd solution by turns, It is difficult for fully infiltrating an aniline, a dopant, and an oxidizing agent to the interior of an anode plate to obtain the solid electrolytic capacitor in which the capacity incidence of a solid electrolytic capacitor will become small, and has necessary electrostatic capacity difficultly consequently.
[0008] Moreover, it is the problem of leakage current especially to become a problem with this kind of solid electrolytic capacitor. Namely, although the dielectric oxide film which sintered the tantalum powder which carried out pressing, formed the sintered compact, and anodized the sintered compact is used as a dielectric when a metal tantalum is used for an anode plate as a valve action metal The specific resistance of the dielectric oxide film is about 1011-ohmcm, and the surface area of a dielectric oxide film is 2 about 10cm 2-1000cm. about 500microA Since the thickness of a dielectric oxide film is about 20nm - 200nm, resistance of a solid electrolytic capacitor serves as abbreviation 100kohm at the maximum, and the leakage current in that case will flow that it is small. Thus, in the conventional solid electrolytic capacitor, leakage current had had the bad influence on the property of a solid electrolytic capacitor greatly.
[0009] Compared with the conventional solid electrolytic capacitor, the place which this invention was made in view of this, and is made into the purpose can reduce leakage current sharply, and is to offer a solid-state electrolytic capacitor with a good property.

[Translation done.]

MEANS

[Means for Solving the Problem] In order to develop that to which this invention person etc. has the large capacity incidence as a solid electrolytic capacitor, and equivalent series resistance and leakage current become small, It is what that the direct conductivity matter contacts the front face of the dielectric oxide film formed by anodic oxidation by making a metal tantalum into an anode plate as a result of inquiring energetically showed clearly that it is the cause of property degradation of leakage current, and resulted in this invention. An insulating layer is formed between a dielectric oxide film and a solid electrolyte, and a solid electrolytic capacitor is formed in it.
[0011] That is, in the solid electrolytic capacitor equipped with the solid electrolyte on the anode plate which consists of a valve action metal, the dielectric oxide film formed in the front face of this anode plate of anodic oxidation, and this dielectric oxide film, this invention prepares an insulating layer between said dielectric oxide films and solid electrolytes, and attains the desired end.
[0012] Moreover, in the solid electrolytic capacitor equipped with the solid electrolyte on the anode plate where this invention consists of a valve action metal, the dielectric oxide film formed in the front face of this anode plate of anodic oxidation, and this dielectric oxide film, specific resistance prepares the insulating layer more than 1012-ohmcm between said dielectric oxide films and solid electrolytes.
[0013] Moreover, said insulating layer is formed in this case with either an epoxy resin, polyimide resin, silicone resin, an unsaturated polyester resin, polystyrene resin, phenol resin, synthetic rubber, thermoplastic elastomer, such mixture or a copolymer. Moreover, it is made to form by the inorganic polymer which includes Si-O-Si association for said insulating layer, or inorganic polymer including aluminum-O-aluminum association.
[0014] Moreover, said solid electrolyte is formed with either the poly aniline, the poly aniline derivative, Pori (p-phenylene), the Pori (p-phenylene) derivative, the poly vinylene, the poly vinylene derivative, polypyrrole, a polypyrrole derivative, the poly thiophene or the poly thiophene derivative.
[0015] Moreover, the anode plate where this invention consists of a valve action metal and the dielectric oxide film formed in the front face of this anode plate, Manufacture of a solid electrolytic capacitor equipped with the solid electrolyte formed on this dielectric oxide film is faced. The 1st process which anodizes the front face of said anode plate and forms said dielectric oxide film, the [which forms an insulating layer after forming a solid electrolyte on the 2nd process which forms an insulating layer on said dielectric oxide film, or said dielectric oxide film] -- it is made to have 2' processes and the 3rd process which forms said solid electrolyte on said insulating layer
[0016] Namely, since the insulating layer is prepared between the dielectric oxide film and the solid electrolyte as it is the solid electrolytic capacitor formed in this way, by this insulating layer, it can be lost that the direct conductivity matter contacts the front face of the dielectric oxide film formed by anodic oxidation, therefore it can reduce leakage current sharply compared with this known kind of solid electrolytic capacitor, and can use it as the solid-state electrolytic capacitor with a good property.
[0017]
[Embodiment of the Invention] In the gestalt of one operation of this invention a solid electrolytic capacitor The anode plate which consists of a valve action metal, and the dielectric oxide film formed in

the front face of an anode plate by anodic oxidation, It has an insulating layer between the conductive polymer layer formed on the dielectric oxide film, and a dielectric oxide film and a conductive polymer layer. A conductive polymer layer The poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), or the Pori (p-phenylene) derivative, Or it is the poly vinylene or the poly vinylene derivative, and specific resistance of an insulating layer is a thing more than 1016-ohmcm preferably more than 1012-ohmcm.
[0018] In the gestalt of other operations of this invention the manufacture approach of a solid electrolytic capacitor The anode plate which consists of a valve action metal, and the dielectric oxide film formed in the front face of an anode plate by anodic oxidation, It is the manufacture approach of the insulating layer formed on the dielectric oxide film, and the solid electrolytic capacitor equipped with the conductive polymer layer on the insulating layer. The 1st process which anodizes the front face of an anode plate and forms a dielectric oxide film, the 2nd process which forms an insulating layer on a dielectric oxide film, On an insulating layer, the poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or it is manufactured respectively through the 3rd process which forms the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), the Pori (p-phenylene) derivative, the poly vinylene, or the poly vinylene derivative.
[0019] The insulating layers formed at the 2nd process are an epoxy resin, phenol resin, polyimide, polystyrene, silicon resin, an unsaturated polyester resin, and synthetic rubber that specific resistance should just be more than 1016-ohmcm preferably more than 1012-ohmcm. In order to form an insulating layer in homogeneity to the interior of a solid electrolytic capacitor component, viscosity is small and the wettability good thing to a dielectric oxide film is desirable.
[0020] The insulating material solution which has the polymerization degree of extent which dissolves the formation approach of the insulating material in the 2nd process in a solvent, In the case of an epoxy resin insulator layer, for example, the bisphenol A mold epoxy resin solution, In the case of a phenol resin insulator layer, in the case of a phenol formaldehyde solution and a polyimide insulator layer, a diamine solution and an acid-anhydride solution, In the case of a silicone resin insulator layer, in the case of an alkoxysilane solution and an unsaturated-polyester-resin insulator layer, a fumaric-acid solution, ethylene glycol, and a styrene solution, In the case of an inorganic polymer insulator layer including Si-O-Si association, a silanol solution, In the case of an inorganic polymer insulator layer including aluminum-O-aluminum association, an alkoxy aluminum solution etc. is adjusted. A dielectric oxide film is immersed in each solution, it heat-treats if needed, the polymerization reaction of an insulating layer is advanced, and specific resistance forms the insulating layer more than 1016-ohmcm on a dielectric oxide film preferably more than 1012-ohmcm.
[0021] About means other than the aforementioned insulating stratification approach On a dielectric oxide film, the poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), or the Pori (p-phenylene) derivative, Or there is the approach of making insulation-ize a solid electrolyte and forming an insulating layer on a dielectric oxide film by forming the solid electrolyte which consists of poly vinylene or a poly vinylene derivative, and heat-treating above the temperature to which the dopant of a solid electrolyte evaporates.

[0022] This purpose can be attained also by inert gas ambient atmospheres, such as nitrogen, being sufficient, and carrying out in a vacuum ambient atmosphere besides performing heat treatment in air. Furthermore, if an insulating layer is formed by this approach, it will become possible to form a uniform insulating layer in a dielectric oxide film front face, and it will become possible to reduce leakage current sharply compared with this known kind of solid electrolytic capacitor.
[0023] In the gestalt of other operations of this invention the manufacture approach of a solid electrolytic capacitor the [which forms an insulating layer after forming a solid electrolyte on the 1st process which anodizes the front face of an anode plate and forms a dielectric oxide film, and a dielectric oxide film] -- 2' processes -- On an insulating layer, the poly aniline, the poly aniline derivative, polypyrrole, or a polypyrrole derivative, Or it is manufactured respectively through the 3rd process which forms the poly thiophene, the poly thiophene derivative, Pori (p-phenylene), the Pori (p-

phenylene) derivative, the poly vinylene, or the poly vinylene derivative.
[0024] the -- in 2' processes, by forming a solid electrolyte on a dielectric oxide film, the electrolytic polymerization reaction on a dielectric oxide film is attained, and an insulating layer is formed on a dielectric oxide film by the electrolytic polymerization reaction. In 2' processes, after forming a solid electrolyte on a dielectric oxide film, an electrolytic polymerization reaction is possible. the [therefore,] -- the monomer solution with which the specific resistance of the insulating layer formed of an electrolytic polymerization reaction becomes more than 1016-ohmcm preferably more than 1012-ohmcm -- adjusting -- the monomer solution -- the, after the dielectric oxide film which formed the solid electrolyte in the front face at 2' processes is immersed By impressing an electrical potential difference and carrying out electrolytic polymerization of the monomer, an insulating layer is formed on a dielectric oxide film.
[0025] The monomer solution is a solution which dissolved the compound which expresses with for example, amino diphenyl or drawing 2 which is represented by the amino benzophenone that the specific resistance of the insulating layer formed by electrolytic polymerization should just be more than 1016-ohmcm preferably more than 1012-ohmcm. According to this approach, by impressing the electric field impressed at the time of electrolytic polymerization to the whole dielectric oxide film, it becomes possible to form a uniform insulating layer in a dielectric oxide-film front face, and it becomes possible to reduce leakage current sharply compared with this known kind of solid electrolytic capacitor.
[0026] This invention is explained to a detail based on the example illustrated below.
[0027] [Example 1] Drawing 1 is the sectional view showing the configuration of one example of the solid electrolytic capacitor by this invention, and shows the example of the tantalum condenser which constituted the anode plate from a sintered compact of a metal tantalum. the anode plate where 1 consists of impalpable powder of a tantalum in drawing 1 , and 2 -- an anode plate lead and 3 -- for a conductive polymer layer and 6, as for an anode terminal and 8, a silver larer and 7 are [a dielectric oxide film and 4 / an insulating layer and 5 / a cathode terminal and 9] sheathing.
[0028] Namely, as for the solid electrolytic capacitor by this invention, the insulating layer 4 is formed between the dielectric oxide film 3 and the conductive polymer layer (solid electrolyte) 5. In addition, as for this insulating layer, specific resistance is formed more than 1012-ohmcm.
[0029] It is as follows when here describes the circumstances in the production process of the solid electrolytic capacitor (tantalum condenser) of this example 1.
[0030] First, it changes into the condition of having inserted in the end section of the anode plate lead 2 into the impalpable powder of a metal tantalum, and pressing is carried out, the acquired Plastic solid is sintered by high temperature in a vacuum, and the anode plate 1 which consists of a sintered compact is formed (the 1st process).
[0031] Next, the anode plate 1 obtained at the 1st process is immersed into an aqua-fortis water solution, chemical conversion is performed after that, and the dielectric oxide film 3 of rated 7V10micro F is formed in anode plate 1 front face (the 2nd process).
[0032] Subsequently, a 0.01M4 and 4'-diamino diphenyl ether NMP (N-methyl-2-pyrrolidone) solution and the NMP solution of 0.01M biphenyl tetracarboxylic dianhydride are adjusted, respectively. Specific resistance forms the insulating layer 4 which consists of polyimide which is about 1016-ohmcm on scaling anode plate 1 front face by heating the anode plate 1 (this being hereafter called scaling anode plate 1) which formed the dielectric oxide film 3 according to the 2nd process at 150 degrees C, after being immersed in each solution by turns (the 3rd process).
[0033] Then, a 0.5M ammonium-peroxydisulfate water solution is adjusted, and the scaling anode plate 1 which formed the insulating layer 4 according to the 3rd process is immersed in a 0.5M ammonium-peroxydisulfate water solution for 10 seconds (the 4th process).
[0034] Next, an equivalent aniline and the water solution of p-phenolsulfonic acid adjust the aniline solution whose concentration is 0.5M. And 30 minutes after the 0.5M ammonium-peroxydisulfate water solution in the 4th process is immersed, the scaling anode plate 1 is immersed in an aniline solution for 10 seconds (the 5th process).
[0035] Subsequently, after the aniline solution in the 5th process is immersed, the scaling anode plate 1

is held at 50 degrees C for 30 minutes, and a chemistry oxidation-polymerization reaction is produced on the scaling anode plate 1 (the 6th process).
[0036] Furthermore, to the scaling anode plate 1 which carried out the circumstances of the 6th process, immersion to said ammonium-peroxydisulfate water solution and immersion to said aniline solution are performed by a unit of 20 times by turns, and the conductive polymer layer 5 obtained by the chemistry oxidation-polymerization reaction on the front face of the scaling anode plate 1 is formed (the 7th process).
[0037] Then, a silver larer 6 is formed in the predetermined part of the scaling anode plate 1 which carried out the circumstances of the 7th process and formed the insulating layer 4 after applying carbon paste and a silver paste (the 8th process).
[0038] Next, an anode terminal 7 is connected conductively to the other end of the anode plate lead 2 by welding after the 8th process, and a cathode terminal 8 is connected to a silver larer 6 (the 9th process).
[0039] Then, after the 9th process is performed, except for the derivation edge of an anode terminal 7 and a cathode terminal 8, resin is applied to the whole by the mold method, and the solid electrolytic capacitor (tantalum condenser) covered with sheathing 9 is formed (the 10th process).
[0040] Here, Table 1 is a table in which impressing rated voltage 7V and showing the leakage current of 1 minute after about the solid electrolytic capacitor (tantalum condenser) of this example 1, and the solid electrolytic capacitor of the example 1 of a comparison separately formed in order to compare with this example 1. A leak current value shows the average of ten solid electrolytic capacitors.
[0041]
[Table 1]

表 1

種類	リーク電流
実施例 1	0.52 μA
実施例 2	0.35 μA
比較例 1	2.3mA

[0042] In Table 1, the leakage current of the solid electrolytic capacitor of this example 1 in which the insulating layer was formed serves as the range of 0.1-1microA, it is an average of 0.52microA, the leakage current of the example 1 of a comparison serves as the range of 1-5mA, and it is an average of 2.3mA. Thus, the leakage current of the solid electrolytic capacitor of this example 1 is reduced sharply.
[0043] By the way, the solid electrolytic capacitor of the example 1 of a comparison for a comparison with this example 1 is manufactured as follows.
[0044] First, in the production process of the solid electrolytic capacitor of this example 1, the solid electrolytic capacitor of the example 1 of a comparison excepts the process which forms an insulating layer 4, i.e., the 3rd process, and is manufactured respectively through the 4th process to the 2nd process and the 10th process from the 1st process.
[0045] [Example 2] Next, the circumstances in the production process of the solid electrolytic capacitor (tantalum condenser) of this example 2 are described. In this example 2, from the 1st process of said this example 1 to the 2nd process is carried out.
[0046] Then, to the scaling anode plate 1 which carried out the circumstances of the 2nd process, like the 7th process of said this example 1, immersion to a ammonium-peroxydisulfate water solution and immersion to said aniline solution are performed by a unit of 5 times by turns, and the conductive polymer layer obtained by the chemistry oxidation-polymerization reaction on the front face of the scaling anode plate 1 is formed (the 3' process).
[0047] next, a 0.05M4-amino benzophenone solution -- adjusting -- the 3' -- after the scaling anode plate 1 which carried out the circumstances of the process and formed the conductive polymer layer is immersed, an insulating layer 4 is formed on the scaling anode plate 1 by impressing and carrying out

electrolytic polymerization of the electrical potential difference to the scaling anode plate 1 (the 4' process).

[0048] subsequently, the 4' -- on the scaling anode plate 1 which carried out the circumstances of the process and formed the insulating layer 4, like the 7th process of said this example 1, immersion to a ammonium-peroxydisulfate water solution and immersion to said aniline solution are performed by a unit of 15 times by turns, and the conductive polymer layer 5 obtained by the front face of the scaling anode plate 1 by the chemistry oxidation-polymerization reaction is formed (the 7' process).

[0049] Subsequently, from the 8th process of said this example 1 to the 10th process is carried out.

[0050] In addition, about the solid electrolytic capacitor (tantalum condenser) of this example 2, rated voltage 7V are impressed to Table 1, and the leakage current of 1 minute after is shown in it. In this table, the leakage current of the solid electrolytic capacitor of this example 2 which formed the insulating layer by the electrolytic polymerization reaction serves as the range of 0.1-0.8microA, it is an average of 0.35microA, and it turns out that leakage current is decreasing sharply to the solid electrolytic capacitor and EQC of this example 1 mentioned above.

[0051] As many things have been explained above, it can be lost that the direct conductivity matter contacts the front face of the dielectric oxide film formed by anodic oxidation by this insulating layer 4 since the insulating layer 4 is formed between the dielectric oxide film 3 and the conductive polymer layer 5, i.e., a solid electrolyte, according to this invention, therefore leakage current can be reduced sharply.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the vertical section side elevation showing one example of the solid electrolytic capacitor of this invention.
[Drawing 2] It is drawing showing the chemical formula of the monomer of the insulating layer of one example of the solid electrolytic capacitor by this invention.
[Description of Notations]
1 [-- An insulating layer, 5 / -- A conductive polymer layer, 6 / -- A silver larer, 7 / -- An anode terminal, 8 / -- A cathode terminal, 9 / -- Sheathing, R1-R11 / -- They are hydrogen, BAROGEN the amino group, a phenyl group, an alkyl group, a carbonyl group, an alkoxyl group, and X independently, respectively. -- Nothing, azo, a phenyl group, an alkyl group, ester group.] -- An anode plate (sintered compact), 2 -- The lead wire for anode plates, 3 -- A dielectric oxide film, 4

[Translation done.]

* NOTICES *

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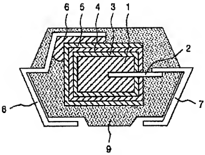
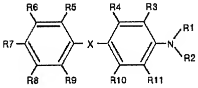
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]
図 1



[Drawing 2]
図 2



[Translation done.]